

**Chapter 19****Ionic Equilibria in Aqueous Systems**

Homework:

**Buffers**

By definition a buffer resists the change in the pH when small amounts of either acid or base are added to the solution. A buffer is an acid-conjugate base or base-conjugate acid chemical system. In the human body buffers are at work constantly to maintain a blood pH of between 6.8 and 7.8. Outside this range life is not possible.

**How Buffers Work: The Common Ion Effect**

When a weak acid is mixed with its conjugate base the pH is moderated some where between the pH expected of either the acid alone or conjugate base alone. Likewise, when a weak base is mixed with its conjugate acid the pH is moderated some where between the pH expected of either the base alone or conjugate acid alone.

This causes a buffering effect that resists a change in the pH. This buffering effect is because both acid and conjugate base are present in the solution. When strong acid is added to the solution, the base reacts with it producing a weak acid. When strong base is added to the solution, the acid reacts with it producing a weak base.

There are several ways to get an acid and conjugate base, or base and conjugate acid in a solution at the same time. One could put a weak acid or base and a salt containing its conjugate in the solution thus creating a buffer, or one could put a weak acid with a strong base, or one could put a weak base with a strong acid. No matter how the solution is created;

- 1 All equilibria must be obeyed simultaneously.
- 2 The stronger acid or base controls the pH.
- 3 Excess strong acid or base controls the pH.
- 4 The final concentrations of species are what control the pH.

Problem:

- a) Design a buffer system having a pH of 3 using acetic acid and sodium acetate.
- b) Calculate the pH for a liter of water to which 1 mL of 1M HCl has been added.
- c) Calculate the pH for a liter of water to which 1 mL of 1M NaOH has been added.
- d) Calculate the pH for a liter of the buffer system created in part a) when 1 mL of 1M HCl has been added.
- e) Calculate the pH for a liter of the buffer system created in part a) when 1 mL of 1M NaOH has been added.

Problem:

Design a buffer having a pH of 8.2.

Problem:

Find the pH of a solution made by adding 30 ml of .5 M HCl to 50 ml of 1 M NH<sub>4</sub>.

Problem:

Find the pH of a solution made by adding .1 moles of HCN and .05 moles of KCN to 100 ml of water.

**Titrations and pH Curves**

Problem: Strong acid-strong base titration

Accurately draw a titration curve for the addition of .1 M NaOH into 10 mL of .1 M HCl. Use 1 mL increments and add a total of 15 mL of base.

Liters	Total V <sub>acid</sub>	Total V <sub>total</sub>	Total mol H <sup>+</sup>	Total mol OH <sup>-</sup>	x <sub>1</sub> mol H <sup>+</sup>	x <sub>1</sub> mol OH <sup>-</sup>	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	pH
0	.010	.010	.001	0	.01	0	.1	$1 \times 10^{-13}$	1
.001	.010	.011	.001	.0001	.0009	0	.08182	$2.22 \times 10^{-13}$	1.09
.002	.010	.012	.001	.0002	.0008	0	.06667		1.14
.003	.010	.013							
.004									

Use a spreadsheet to finish filling out all data up to 15mL of base added and draw an accurate pH vs mL base graph.

Problems to consider for your graph.

- a) On your graphs clearly show the equivalence point.
- b) Find the pH at 5 ml. (The half equivalence point) This should be no surprise.
- c) What indicator(s) should be used for the neutralization of this strong acid.
- d) Is there any buffering effect for the titration of a strong acid-strong base titration?

Problem: Weak acid-strong base titration

Accurately draw a titration curve for the addition of .1 M NaOH into 10 mL of .1 M HOAc.  $K_a = 1.8 \times 10^{-5}$ . Use 1 mL increments and add a total of 15 mL of base.
Liters	Mole V<sub>base</sub>	Mole V<sub>total</sub>	Mole HOAc	Mole OH<sup>-</sup>	x<sub>1</sub> mole HOAc	x<sub>1</sub> mole OH<sup>-</sup>	x<sub>2</sub> mole HOAc	x<sub>2</sub> mole OH<sup>-</sup>	x<sub>3</sub> mole HOAc	x<sub>3</sub> mole OH<sup>-</sup>	x<sub>4</sub> mole HOAc	x<sub>4</sub> mole OH<sup>-</sup>	x<sub>5</sub> mole HOAc	x<sub>5</sub> mole OH<sup>-</sup>	x<sub>6</sub> mole HOAc	x<sub>6</sub> mole OH<sup>-</sup>	x<sub>7</sub> mole HOAc	x<sub>7</sub> mole OH<sup>-</sup>	x<sub>8</sub> mole HOAc	x<sub>8</sub> mole OH<sup>-</sup>	x<sub>9</sub> mole HOAc	x<sub>9</sub> mole OH<sup>-</sup>	x<sub>10</sub> mole HOAc	x<sub>10</sub> mole OH<sup>-</sup>	x<sub>11</sub> mole HOAc	x<sub>11</sub> mole OH<sup>-</sup>	x<sub>12</sub> mole HOAc	x<sub>12</sub> mole OH<sup>-</sup>	x<sub>13</sub> mole HOAc	x<sub>13</sub> mole OH<sup>-</sup>	x<sub>14</sub> mole HOAc	x<sub>14</sub> mole OH<sup>-</sup>	x<sub>15</sub> mole HOAc	x<sub>15</sub> mole OH<sup>-</sup>	x<sub>16</sub> mole HOAc	x<sub>16</sub> mole OH<sup>-</sup>	x<sub>17</sub> mole HOAc	x<sub>17</sub> mole OH<sup>-</sup>	x<sub>18</sub> mole HOAc	x<sub>18</sub> mole OH<sup>-</sup>	x<sub>19</sub> mole HOAc	x<sub>19</sub> mole OH<sup>-</sup>	x<sub>20</sub> mole HOAc	x<sub>20</sub> mole OH<sup>-</sup>	x<sub>21</sub> mole HOAc	x<sub>21</sub> mole OH<sup>-</sup>	x<sub>22</sub> mole HOAc	x<sub>22</sub> mole OH<sup>-</sup>	x<sub>23</sub> mole HOAc	x<sub>23</sub> mole OH<sup>-</sup>	x<sub>24</sub> mole HOAc	x<sub>24</sub> mole OH<sup>-</sup>	x<sub>25</sub> mole HOAc	x<sub>25</sub> mole OH<sup>-</sup>	x<sub>26</sub> mole HOAc	x<sub>26</sub> mole OH<sup>-</sup>	x<sub>27</sub> mole HOAc	x<sub>27</sub> mole OH<sup>-</sup>	x<sub>28</sub> mole HOAc	x<sub>28</sub> mole OH<sup>-</sup>	x<sub>29</sub> mole HOAc	x<sub>29</sub> mole OH<sup>-</sup>	x<sub>30</sub> mole HOAc	x<sub>30</sub> mole OH<sup>-</sup>	x<sub>31</sub> mole HOAc	x<sub>31</sub> mole OH<sup>-</sup>	x<sub>32</sub> mole HOAc	x<sub>32</sub> mole OH<sup>-</sup>	x<sub>33</sub> mole HOAc	x<sub>33</sub> mole OH<sup>-</sup>	x<sub>34</sub> mole HOAc	x<sub>34</sub> mole OH<sup>-</sup>	x<sub>35</sub> mole HOAc	x<sub>35</sub> mole OH<sup>-</sup>	x<sub>36</sub> mole HOAc	x<sub>36</sub> mole OH<sup>-</sup>	x<sub>37</sub> mole HOAc	x<sub>37</sub> mole OH<sup>-</sup>	x<sub>38</sub> mole HOAc	x<sub>38</sub> mole OH<sup>-</sup>	x<sub>39</sub> mole HOAc	x<sub>39</sub> mole OH<sup>-</sup>	x<sub>40</sub> mole HOAc	x<sub>40</sub> mole OH<sup>-</sup>	x<sub>41</sub> mole HOAc	x<sub>41</sub> mole OH<sup>-</sup>	x<sub>42</sub> mole HOAc	x<sub>42</sub> mole OH<sup>-</sup>	x<sub>43</sub> mole HOAc	x<sub>43</sub> mole OH<sup>-</sup>	x<sub>44</sub> mole HOAc	x<sub>44</sub> mole OH<sup>-</sup>	x<sub>45</sub> mole HOAc	x<sub>45</sub> mole OH<sup>-</sup>	x<sub>46</sub> mole HOAc	x<sub>46</sub> mole OH<sup>-</sup>	x<sub>47</sub> mole HOAc	x<sub>47</sub> mole OH<sup>-</sup>	x<sub>48</sub> mole HOAc	x<sub>48</sub> mole OH<sup>-</sup>	x<sub>49</sub> mole HOAc	x<sub>49</sub> mole OH<sup>-</sup>	x<sub>50</sub> mole HOAc	x<sub>50</sub> mole OH<sup>-</sup>	x<sub>51</sub> mole HOAc	x<sub>51</sub> mole OH<sup>-</sup>	x<sub>52</sub> mole HOAc	x<sub>52</sub> mole OH<sup>-</sup>	x<sub>53</sub> mole HOAc	x<sub>53</sub> mole OH<sup>-</sup>	x<sub>54</sub> mole HOAc	x<sub>54</sub> mole OH<sup>-</sup>	x<sub>55</sub> mole HOAc	x<sub>55</sub> mole OH<sup>-</sup>	x<sub>56</sub> mole HOAc	x<sub>56</sub> mole OH<sup>-</sup>	x<sub>57</sub> mole HOAc	x<sub>57</sub> mole OH<sup>-</sup>	x<sub>58</sub> mole HOAc	x<sub>58</sub> mole OH<sup>-</sup>	x<sub>59</sub> mole HOAc	x<sub>59</sub> mole OH<sup>-</sup>	x<sub>60</sub> mole HOAc	x<sub>60</sub> mole OH<sup>-</sup>	x<sub>61</sub> mole HOAc	x<sub>61</sub> mole OH<sup>-</sup>	x<sub>62</sub> mole HOAc	x<sub>62</sub> mole OH<sup>-</sup>	x<sub>63</sub> mole HOAc	x<sub>63</sub> mole OH<sup>-</sup>	x<sub>64</sub> mole HOAc	x<sub>64</sub> mole OH<sup>-</sup>	x<sub>65</sub> mole HOAc	x<sub>65</sub> mole OH<sup>-</sup>	x<sub>66</sub> mole HOAc	x<sub>66</sub> mole OH<sup>-</sup>	x<sub>67</sub> mole HOAc	x<sub>67</sub> mole OH<sup>-</sup>	x<sub>68</sub> mole HOAc	x<sub>68</sub> mole OH<sup>-</sup>	x<sub>69</sub> mole HOAc	x<sub>69</sub> mole OH<sup>-</sup>	x<sub>70</sub> mole HOAc	x<sub>70</sub> mole OH<sup>-</sup>	x<sub>71</sub> mole HOAc	x<sub>71</sub> mole OH<sup>-</sup>	x<sub>72</sub> mole HOAc	x<sub>72</sub> mole OH<sup>-</sup>	x<sub>73</sub> mole HOAc	x<sub>73</sub> mole OH<sup>-</sup>	x<sub>74</sub> mole HOAc	x<sub>74</sub> mole OH<sup>-</sup>	x<sub>75</sub> mole HOAc	x<sub>75</sub> mole OH<sup>-</sup>	x<sub>76</sub> mole HOAc	x<sub>76</sub> mole OH<sup>-</sup>	x<sub>77</sub> mole HOAc	x<sub>77</sub> mole OH<sup>-</sup>	x<sub>78</sub> mole HOAc	x<sub>78</sub> mole OH<sup>-</sup>	x<sub>79</sub> mole HOAc	x<sub>79</sub> mole OH<sup>-</sup>	x<sub>80</sub> mole HOAc	x<sub>80</sub> mole OH<sup>-</sup>	x<sub>81</sub> mole HOAc	x<sub>81</sub> mole OH<sup>-</sup>	x<sub>82</sub> mole HOAc	x<sub>82</sub> mole OH<sup>-</sup>	x<sub>83</sub> mole HOAc	x<sub>83</sub> mole OH<sup>-</sup>	x<sub>84</sub> mole HOAc	x<sub>84</sub> mole OH<sup>-</sup>	x<sub>85</sub> mole HOAc	x<sub>85</sub> mole OH<sup>-</sup>	x<sub>86</sub> mole HOAc	x<sub>86</sub> mole OH<sup>-</sup>	x<sub>87</sub> mole HOAc	x<sub>87</sub> mole OH<sup>-</sup>	x<sub>88</sub> mole HOAc	x<sub>88</sub> mole OH<sup>-</sup>	x<sub>89</sub> mole HOAc	x<sub>89</sub> mole OH<sup>-</sup>	x<sub>90</sub> mole HOAc	x<sub>90</sub> mole OH<sup>-</sup>	x<sub>91</sub> mole HOAc	x<sub>91</sub> mole OH<sup>-</sup>	x<sub>92</sub> mole HOAc	x<sub>92</sub> mole OH<sup>-</sup>	x<sub>93</sub> mole HOAc	x<sub>93</sub> mole OH<sup>-</sup>	x<sub>94</sub> mole HOAc	x<sub>94</sub> mole OH<sup>-</sup>	x<sub>95</sub> mole HOAc	x<sub>95</sub> mole OH<sup>-</sup>	x<sub>96</sub> mole HOAc	x<sub>96</sub> mole OH<sup>-</sup>	x<sub>97</sub> mole HOAc	x<sub>97</sub> mole OH<sup>-</sup>	x<sub>98</sub> mole HOAc	x<sub>98</sub> mole OH<sup>-</sup>	x<sub>99</sub> mole HOAc	x<sub>99</sub> mole OH<sup>-</sup>	x<sub>100</sub> mole HOAc	x<sub>100</sub> mole OH<sup>-</sup>	x<sub>101</sub> mole HOAc	x<sub>101</sub> mole OH<sup>-</sup>	x<sub>102</sub> mole HOAc	x<sub>102</sub> mole OH<sup>-</sup>	x<sub>103</sub> mole HOAc	x<sub>103</sub> mole OH<sup>-</sup>	x<sub>104</sub> mole HOAc	x<sub>104</sub> mole OH<sup>-</sup>	x<sub>105</sub> mole HOAc	x<sub>105</sub> mole OH<sup>-</sup>	x<sub>106</sub> mole HOAc	x<sub>106</sub> mole OH<sup>-</sup>	x<sub>107</sub> mole HOAc	x<sub>107</sub> mole OH<sup>-</sup>	x<sub>108</sub> mole HOAc	x<sub>108</sub> mole OH<sup>-</sup>	x<sub>109</sub> mole HOAc	x<sub>109</sub> mole OH<sup>-</sup>	x<sub>110</sub> mole HOAc	x<sub>110</sub> mole OH<sup>-</sup>	x<sub>111</sub> mole HOAc	x<sub>111</sub> mole OH<sup>-</sup>	x<sub>112</sub> mole HOAc	x<sub>112</sub> mole OH<sup>-</sup>	x<sub>113</sub> mole HOAc	x<sub>113</sub> mole OH<sup>-</sup>	x<sub>114</sub> mole HOAc	x<sub>114</sub> mole OH<sup>-</sup>	x<sub>115</sub> mole HOAc	x<sub>115</sub> mole OH<sup>-</sup>	x<sub>116</sub> mole HOAc	x<sub>116</sub> mole OH<sup>-</sup>	x<sub>117</sub> mole HOAc	x<sub>117</sub> mole OH<sup>-</sup>	x<sub>118</sub> mole HOAc	x<sub>118</sub> mole OH<sup>-</sup>	x<sub>119</sub> mole HOAc	x<sub>119</sub> mole OH<sup>-</sup>	x<sub>120</sub> mole HOAc	x<sub>120</sub> mole OH<sup>-</sup>	x<sub>121</sub> mole HOAc	x<sub>121</sub> mole OH<sup>-</sup>	x<sub>122</sub> mole HOAc	x<sub>122</sub> mole OH<sup>-</sup>	x<sub>123</sub> mole HOAc	x<sub>123</sub> mole OH<sup>-</sup>	x<sub>124</sub> mole HOAc	x<sub>124</sub> mole OH<sup>-</sup>	x<sub>125</sub> mole HOAc	x<sub>125</sub> mole OH<sup>-</sup>	x<sub>126</sub> mole HOAc	x<sub>126</sub> mole OH<sup>-</sup>	x<sub>127</sub> mole HOAc	x<sub>127</sub> mole OH<sup>-</sup>	x<sub>128</sub> mole HOAc	x<sub>128</sub> mole OH<sup>-</sup>	x<sub>129</sub> mole HOAc	x<sub>129</sub> mole OH<sup>-</sup>	x<sub>130</sub> mole HOAc	x<sub>130</sub> mole OH<sup>-</sup>	x<sub>131</sub> mole HOAc	x<sub>131</sub> mole OH<sup>-</sup>	x<sub>132</sub> mole HOAc	x<sub>132</sub> mole OH<sup>-</sup>	x<sub>133</sub> mole HOAc	x<sub>133</sub> mole OH<sup>-</sup>	x<sub>134</sub> mole HOAc	x<sub>134</sub> mole OH<sup>-</sup>	x<sub>135</sub> mole HOAc	x<sub>135</sub> mole OH<sup>-</sup>	x<sub>136</sub> mole HOAc	x<sub>136</sub> mole OH<sup>-</sup>	x<sub>137</sub> mole HOAc	x<sub>137</sub> mole OH<sup>-</sup>	x<sub>138</sub> mole HOAc	x<sub>138</sub> mole OH<sup>-</sup>	x<sub>139</sub> mole HOAc	x<sub>139</sub> mole OH<sup>-</sup>	x<sub>140</sub> mole HOAc	x<sub>140</sub> mole OH<sup>-</sup>	x<sub>141</sub> mole HOAc	x<sub>141</sub> mole OH<sup>-</sup>	x<sub>142</sub> mole HOAc	x<sub>142</sub> mole OH<sup>-</sup>	x<sub>143</sub> mole HOAc	x<sub>143</sub> mole OH<sup>-</sup>	x<sub>144</sub> mole HOAc	x<sub>144</sub> mole OH<sup>-</sup>	x<sub>145</sub> mole HOAc	x<sub>145</sub> mole OH<sup>-</sup>	x<sub>146</sub> mole HOAc	x<sub>146</sub> mole OH<sup>-</sup>	x<sub>147</sub> mole HOAc	x<sub>147</sub> mole OH<sup>-</sup>	x<sub>148</sub> mole HOAc	x<sub>148</sub> mole OH<sup>-</sup>	x<sub>149</sub> mole HOAc	x<sub>149</sub> mole OH<sup>-</sup>	x<sub>150</sub> mole HOAc	x<sub>150</sub> mole OH<sup>-</sup>	x<sub>151</sub> mole HOAc	x<sub>151</sub> mole OH<sup>-</sup>	x<sub>152</sub> mole HOAc	x<sub>152</sub> mole OH<sup>-</sup>	x<sub>153</sub> mole HOAc	x<sub>153</sub> mole OH<sup>-</sup>	x<sub>154</sub> mole HOAc	x<sub>154</sub> mole OH<sup>-</sup>	x<sub>155</sub> mole HOAc	x<sub>155</sub> mole OH<sup>-</sup>	x<sub>156</sub> mole HOAc	x<sub>156</sub> mole OH<sup>-</sup>	x<sub>157</sub> mole HOAc	x<sub>157</sub> mole OH<sup>-</sup>	x<sub>158</sub> mole HOAc	x<sub>158</sub> mole OH<sup>-</sup>	x<sub>159</sub> mole HOAc	x<sub>159</sub> mole OH<sup>-</sup>	x<sub>160</sub> mole HOAc	x<sub>160</sub> mole OH<sup>-</sup>	x<sub>161</sub> mole HOAc	x<sub>161</sub> mole OH<sup>-</sup>	x<sub>162</sub> mole HOAc	x<sub>162</sub> mole OH<sup>-</sup>	x<sub>163</sub> mole HOAc	x<sub>163</sub> mole OH<sup>-</sup>	x<sub>164</sub> mole HOAc	x<sub>164</sub> mole OH<sup>-</sup>	x<sub>165</sub> mole HOAc	x<sub>165</sub> mole OH<sup>-</sup>	x<sub>166</sub> mole HOAc	x<sub>166</sub> mole OH<sup>-</sup>	x<sub>167</sub> mole HOAc	x<sub>167</sub> mole OH<sup>-</sup>	x<sub>168</sub> mole HOAc	x<sub>168</sub> mole OH<sup>-</sup>	x<sub>169</sub> mole HOAc	x<sub>169</sub> mole OH<sup>-</sup>	x<sub>170</sub> mole HOAc	x<sub>170</sub> mole OH<sup>-</sup>	x<sub>171</sub> mole HOAc	x<sub>171</sub> mole OH<sup>-</sup>	x<sub>172</sub> mole HOAc	x<sub>172</sub> mole OH<sup>-</sup>	x<sub>173</sub> mole HOAc	x<sub>173</sub> mole OH<sup>-</sup>	x<sub>174</sub> mole HOAc	x<sub>174</sub> mole OH<sup>-</sup>	x<sub>175</sub> mole HOAc	x<sub>175</sub> mole OH<sup>-</sup>	x<sub>176</sub> mole HOAc	x<sub>176</sub> mole OH<sup>-</sup>	x<sub>177</sub> mole HOAc	x<sub>177</sub> mole OH<sup>-</sup>	x<sub>178</sub> mole HOAc	x<sub>178</sub> mole OH<sup>-</sup>	x<sub>179</sub> mole HOAc	x<sub>179</sub> mole OH<sup>-</sup>	x<sub>180</sub> mole HOAc	x<sub>180</sub> mole OH<sup>-</sup>	x<sub>181</sub> mole HOAc	x<sub>181</sub> mole OH<sup>-</sup>	x<sub>182</sub> mole HOAc	x<sub>182</sub> mole OH<sup>-</sup>	x<sub>183</sub> mole HOAc	x<sub>183</sub> mole OH<sup>-</sup>	x<sub>184</sub> mole HOAc	x<sub>184</sub> mole OH<sup>-</sup>	x<sub>185</sub> mole HOAc	x<sub>185</sub> mole OH<sup>-</sup>	x<sub>186</sub> mole HOAc	x<sub>186</sub> mole OH<sup>-</sup>	x<sub>187</sub> mole HOAc	x<sub>187</sub> mole OH<sup>-</sup>	x<sub>188</sub> mole HOAc	x<sub>188</sub> mole OH<sup>-</sup>	x<sub>189</sub> mole HOAc	x<sub>189</sub> mole OH<sup>-</sup>	x<sub>190</sub> mole HOAc	x<sub>190</sub> mole OH<sup>-</sup>	x<sub>191</sub> mole HOAc	x<sub>191</sub> mole OH<sup>-</sup>	x<sub>192</sub> mole HOAc	x<sub>192</sub> mole OH<sup>-</sup>	x<sub>193</sub> mole HOAc	x<sub>193</sub> mole OH<sup>-</sup>	x<sub>194</sub> mole HOAc	x<sub>194</sub> mole OH<sup>-</sup>	x<sub>195</sub> mole HOAc	x<sub>195</sub> mole OH<sup>-</sup>	x<sub>196</sub> mole HOAc	x<sub>196</sub> mole OH<sup>-</sup>	x<sub>197</sub> mole HOAc	x<sub>197</sub> mole OH<sup>-</sup>	x<sub>198</sub> mole HOAc	x<sub>198</sub> mole OH<sup>-</sup>	x<sub>199</sub> mole HOAc	x<sub>199</sub> mole OH<sup>-</sup>	x<sub>200</sub> mole HOAc	x<sub>200</sub> mole OH<sup>-</sup>	x<sub>201</sub> mole HOAc	x<sub>201</sub> mole OH<sup>-</sup>	x<sub>202</sub> mole HOAc	x<sub>202</sub> mole OH<sup>-</sup>	x<sub>203</sub> mole HOAc	x<sub>203</sub> mole OH<sup>-</sup>	x<sub>204</sub> mole HOAc	x<sub>204</sub> mole OH<sup>-</sup>	x<sub>205</sub> mole HOAc	x<sub>205</sub> mole OH<sup>-</sup>	x<sub>206</sub> mole HOAc	x<sub>206</sub> mole OH<sup>-</sup>	x<sub>207</sub> mole HOAc	x<sub>207</sub> mole OH<sup>-</sup>	x<sub>208</sub> mole HOAc	x<sub>208</sub> mole OH<sup>-</sup>	x<sub>209</sub> mole HOAc	x<sub>209</sub> mole OH<sup>-</sup>	x<sub>210</sub> mole HOAc	x<sub>210</sub> mole OH<sup>-</sup>	x<sub>211</sub> mole HOAc	x<sub>211</sub> mole OH<sup>-</sup>	x<sub>212</sub> mole HOAc	x<sub>212</sub> mole OH<sup>-</sup>	x<sub>213</sub> mole HOAc	x<sub>213</sub> mole OH<sup>-</sup>	x<sub>214</sub> mole HOAc	x<sub>214</sub> mole OH<sup>-</sup>	x<sub>215</sub> mole HOAc	x<sub>215</sub> mole OH<sup>-</sup>	x<sub>216</sub> mole HOAc	x<sub>216</sub> mole OH<sup>-</sup>	x<sub>217</sub> mole HOAc	x<sub>217</sub> mole OH<sup>-</sup>	x<sub>218</sub> mole HOAc	x<sub>218</sub> mole OH<sup>-</sup>	x<sub>219</sub> mole HOAc	x<sub>219</sub> mole OH<sup>-</sup>	x<sub>220</sub> mole HOAc	x<sub>220</sub> mole OH<sup>-</sup>	x<sub>221</sub> mole HOAc	x<sub>221</sub> mole OH<sup>-</sup>	x<sub>222</sub> mole HOAc	x<sub>222</sub> mole OH<sup>-</sup>	x<sub>223</sub> mole HOAc	x<sub>223</sub> mole OH<sup>-</sup>	x<sub>224</sub> mole HOAc	x<sub>224</sub> mole OH<sup>-</sup>	x<sub>225</sub> mole HOAc	x<sub>225</sub> mole OH<sup>-</sup>	x<sub>226</sub> mole HOAc	x<sub>226</sub> mole OH<sup>-</sup>	x<sub>227</sub> mole HOAc	x<sub>227</sub> mole OH<sup>-</sup>	x<sub>228</sub> mole HOAc	x<sub>228</sub> mole OH<sup>-</sup>	x<sub>229</sub> mole HOAc	x<sub>229</sub> mole OH<sup>-</sup>	x<sub>230</sub> mole HOAc	x<sub>230</sub> mole OH<sup>-</sup>	x<sub>231</sub> mole HOAc	x<sub>231</sub> mole OH<sup>-</sup>	x<sub>232</sub> mole HOAc	x<sub>232</sub> mole OH<sup>-</sup>	x<sub>233</sub> mole HOAc	x<sub>233</sub> mole OH<sup>-</sup>	x<sub>234</sub> mole

c) Find the  $[H^+]$  at the half equivalents point. Does this look familiar?  
 d) Prove that  $K_a = [H^+]$  at the half equivalents point.  
 e) What indicators should be used for a neutralization titration for this acid.  
 f) Clearly indicate the buffer region on the graph.

**The Henderson-Hasselbalch Equation**

$$pH = pK_a + \log([base]/[acid])$$

Problem:

Use the Henderson-Hasselbalch equation to calculate the pH at the one fourth equivalents point for your acetic acid - sodium hydroxide graph; i.e. 2.5 mL NaOH added.

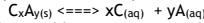
**Solubility Product Constant ( $K_{sp}$ )**

When a salt dissolves in water the ions dissociate and are present in solution in the same proportions found in the salt.



Note: C=cation, A=anions, and x & y are the subscripts for the salt.

When a salt is saturated or the salt is only slightly soluble in water, an equilibrium is set up between the solid and aqueous phases of the salt.



The equilibrium expression for this process is:

$$K_{sp} = [C_{(aq)}]^x[A_{(aq)}]^y / [C_xA_y(s)]$$

The concentration of the solid phase has no physical meaning and is assigned a constant value of 1. This leads to the general expression for the solubility product:

$$Q_{sp} = [\text{Cations}]^x[\text{Anions}]^y \text{ which equals } K_{sp} \text{ at saturation.}$$

If  $[\text{Cations}]^x[\text{Anions}]^y < K_{sp}$  the solution is unsaturated and can dissolve more solid. If  $[\text{Cations}]^x[\text{Anions}]^y = K_{sp}$  the solution is saturated and no more solid can dissolve. If  $[\text{Cations}]^x[\text{Anions}]^y > K_{sp}$  the solution is supersaturated and precipitation will occur until saturation is reached.

Problem:

Write the  $K_{sp}$  expressions for  $\text{AgCl}$  and  $\text{Ag}_2\text{CrO}_4$ . Which salt  $\text{AgCl}$  or  $\text{Ag}_2\text{CrO}_4$  will form a more concentrated saturated solution?  $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$ ,  $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.1 \times 10^{-12}$

Problem:

a) How many grams of  $\text{PbCl}_2$  can dissolve in 100 g of water?  $K_{sp} = 1.6 \times 10^{-5}$ .  
 b) What must the chloride concentration be brought to in order to reduce the  $[\text{Pb}^{2+}]$  to half the saturation level?

Problem:

A solution is .2 M  $\text{Pb}(\text{NO}_3)_2$ . How many grams of  $\text{NaCl}$  need to be added to this solution to lower the  $\text{Pb}^{2+}$  concentration to .001 M?

Problem:

What is the maximum concentration of chloride that can exist in a .1 M  $\text{AgNO}_3$  solution and not cause any precipitation?

Problem:

What concentration of sulfide must be present to make a maximum separation of zinc ions and copper ions? Assume that both concentrations are .1 M initially.  $K_{sp}(\text{ZnS}) = 1.1 \times 10^{-21}$ ,  $K_{sp}(\text{CuS}) = 6 \times 10^{-36}$

Problem:

What percent of copper ions was removed in the above problem?

Problem:

$\text{H}_2\text{S}(g)$  is soluble in water to the extent of .1 M at 1 atm. What must the pH be in order to make the maximum separation of zinc ions and copper ions? Assume that both concentrations are .1 M initially.  $K_{a1}K_{a2} = K_{\text{H2S}} = 1.1 \times 10^{-20}$

**Effect of pH on Solubility**

For many reactions, the equilibrium will be shifted by the addition of either acid or base. The  $\text{H}^+$  or  $\text{OH}^-$  may react directly with one of the ionic species of the salt or may set up another equilibrium, which increases or decreases the concentration of one of the ionic species. Here are examples of each.

Problem:

At what pH will a solution of .1 M  $\text{AlCl}_3$  give precipitation?  $K_{sp} = 4.6 \times 10^{-33}$

Problem:

$\text{CaC}_2\text{O}_4$  is relatively insoluble in neutral and basic solutions; however in acidic solutions it becomes much more soluble. Determine the solubility of  $\text{CaC}_2\text{O}_4$  in 1 liter of water when the pH has been adjusted to 7 and then adjusted to 2.  $K_{sp} = 2.3 \times 10^{-9}$ ,  $K_{a1}K_{a2} = K_{\text{H2C2O4}} = 2.86 \times 10^{-6}$

From this example, you can see that all equilibria must be simultaneously satisfied.

**Complex-Ion Equilibria**

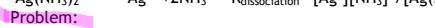
A complex ion is an ion formed by attaching electron pair donors called ligands to metal ions. A brief list of ligands:  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ . One thing that all ligands have in common is a pair of electrons to donate to the central ion.

We treat complex-ion equilibria just like any other equilibrium; however, we may think of the equilibria as either formation of complex ions or the dissociation of complex ions. Consider the formation of silver ammine complex:



$K_{\text{formation}} = [\text{Ag}(\text{NH}_3)_2^+]/[\text{Ag}^+][\text{NH}_3]^2$

Consider the dissociation of the silver ammine complex:

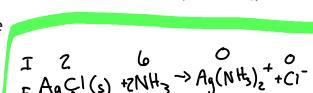
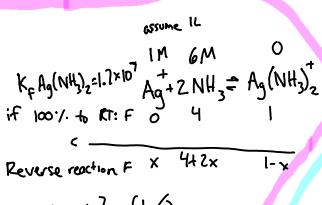
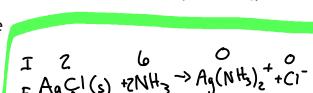
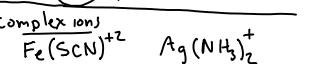
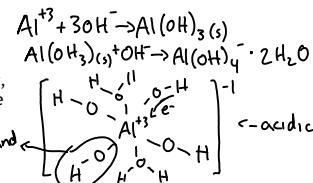


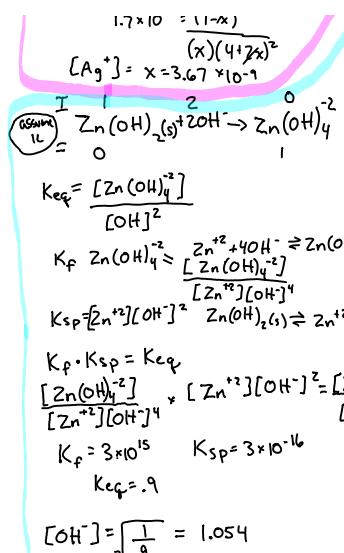
Problem: .1 moles of  $\text{AgNO}_3$  is dissolved in 100 mL of 6 M  $\text{NH}_3$ . What is the  $[\text{Ag}^+]$ ?

Problem:

At what pH will 1 mole of  $\text{Zn}(\text{OH})_2$  completely dissolve in 1 L to form the  $\text{Zn}(\text{OH})_4^{2-}$  complex?

It is a general rule that all equilibria must be obeyed



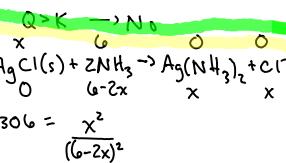
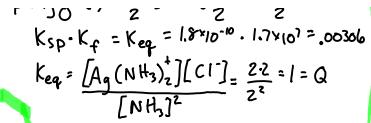
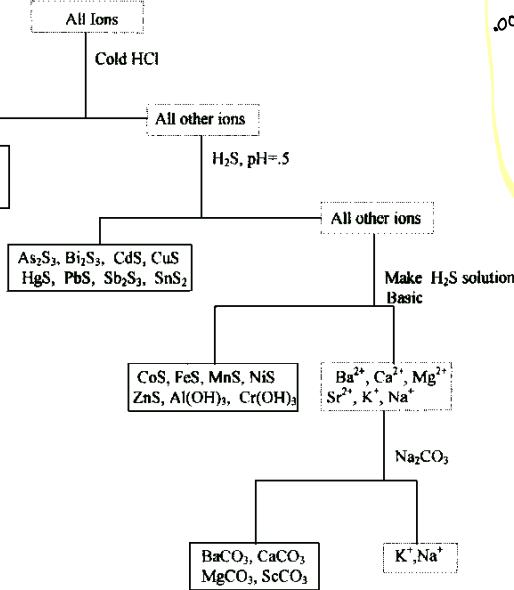


simultaneously. Consider the interplay between the complex-ion equilibria and solubility equilibria for the insoluble salt,  $AgCl$ , and the stable complex,  $Ag(NH_3)_2^+$ :

Problem:

Will 2 moles of  $AgCl$  dissolve in 100 mL of 6 M  $NH_3$ ?

### Application of Solubility Equilibria in Qualitative Chemical Analysis



$$6\sqrt{.00306 \times 10^{-3}} + 2\sqrt{3.06 \times 10^{-3}}x = x$$

$$x = .299$$

$x = \text{amt } AgCl(s) \text{ dissolved in 1L}$   
 $\text{in 100 mL} = .0299 \text{ mole}$

Pasted from <http://fp.academic.venturacollege.edu/doliver/chem1b/notes/Chap19new.htm>

114)  $KCl \quad 3.7 \text{ M} @ 25^\circ\text{C} \quad 100 \text{ mL}$

100mL 6M HCl  
100mL 12M HCl

$$K_{sp} = [K^+][Cl^-] = (3.7 \text{ M})(3.7 \text{ M}) = 13.69$$

$$13.69 = \left(\frac{3.7}{2}\right) \left(\frac{3.7 + 6}{2}\right) = Q = 8.97$$

$Q < K$  no precipitate

$$13.69 = \left(\frac{3.7}{2}\right) \left(\frac{3.7 + 1.2}{2}\right) = 14.5$$

$Q > K$

How much precipitates?

$$K_{sp} = [K^+][Cl^-]$$

$$13.69 = \left(\frac{3.7}{2}\right)(x)$$

$x = 7.4 \text{ M } Cl^- \text{ c-total that can dissolve}$



$$13.69 = (1.85-x)(7.85-x)$$

$$0 = x^2 - 9.7x + .8325$$

$$x = \frac{9.7 \pm \sqrt{9.7^2 - 4(.8325)}}{2}$$

$$x = 0.08869 \text{ M}$$

$$\frac{.008869 \text{ mol}}{1 \text{ L}} \times .200 \text{ L} \times \frac{74.55 \text{ g } KCl}{1 \text{ mol}} = \boxed{1 \text{ g}}$$